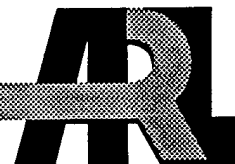


ARMY RESEARCH LABORATORY



New Substrate/Buffer Layer Compounds for
High Temperature Superconductor
Epitaxial Film Growth

Arthur Tauber
Steven C. Tidrow
William D. Wilber
Robert D. Finnegan

ARL-TR-929

May 1996

19960509 102

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

DTIC QUALITY INSPECTED 1

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government endorsement or approval of commercial products or services referenced herein.

| | | | | |
|---|--|---|--|--|
| REPORT DOCUMENTATION PAGE | | | Form Approved OMB NO. 0704-0188 | |
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503. | | | | |
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE May 1996 | | 3. REPORT TYPE AND DATES COVERED Technical Report: Dec 95 to Apr 96 |
| 4. TITLE AND SUBTITLE NEW SUBSTRATE/BUFFER LAYER COMPOUNDS FOR HIGH TEMPERATURE SUPERCONDUCTOR EPITAXIAL FILM GROWTH | | | 5. FUNDING NUMBERS PR: 611102 PE: H94 | |
| 6. AUTHOR(S) Arthur Tauber,* Steven C. Tidrow, William D. Wilber and Robert D. Finnegan | | | | |
| 7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) US Army Research Laboratory (ARL) Physical Sciences Directorate (PSD) ATTN: AMSRL-PS-PC Fort Monmouth, NJ 07703-5601 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-929 | |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | | 10. SPONSORING / MONITORING AGENCY REPORT NUMBER | |
| 11. SUPPLEMENTARY NOTES *Arthur Tauber is with Geo-Centers Inc., 615 Hope Road, Eatontown, NJ 07703. | | | | |
| 12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. | | | 12 b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) A series of compounds in the system A4MeSb012, where A=Ba,Sr and ME=Li,Na and K, were prepared by solid state reaction at elevated temperature. A new form of strontium sodium antimonate (Sr4NaSb3012) was prepared. The compounds that were prepared were characterized with regard to their lattice parameter, density and dielectric properties. Thin films were prepared by pulsed laser ablation deposition from dense targets, and epitaxial relationships identified between YBCO and these compounds. | | | | |
| 14. SUBJECT TERMS High temperature superconductors; HTSC; microwave equipment; A4MeSb3012 substrates; buffers; thin films; epitaxial growth | | | 15. NUMBER OF PAGES 12 | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT UL | |

CONTENTS

| | <u>Page</u> |
|-------------------|-------------|
| INTRODUCTION..... | 1 |
| EXPERIMENTAL..... | 1 |
| RESULTS..... | 3 |
| CONCLUSION..... | 5 |
| REFERENCES | 6 |

LIST OF TABLES

| | |
|--|---|
| TABLE 1. PROPERTIES of $A_4MeSb_3O_{12}$ COMPOUNDS | 2 |
| TABLE 2. DEPOSITION PARAMETERS..... | 2 |
| TABLE 3. OBSERVED X-RAY REFLECTIONS..... | 4 |

NEW SUBSTRATE/BUFFER LAYER COMPOUNDS FOR HIGH TEMPERATURE SUPERCONDUCTOR EPITAXIAL FILM GROWTH

INTRODUCTION

The best superconducting electronic devices have been fabricated as thin film epitaxial structures deposited on dielectric substrates or buffer layers. To achieve high quality films, dielectric substrates/buffer layers must meet stringent requirements. [1 -5]. Most devices described in the literature have been deposited on lanthanum aluminate (LaAlO_3) or magnesium oxide (MgO) substrates and buffered yttrium stabilized zirconia (YSZ) or sapphire, all of which have some drawbacks. LaAlO_3 has a dielectric constant in the range 22- 24 which means at high frequency (> 12 GHz) device features become unmanageably small. Furthermore this compound is rhombohedral creating difficult device calculations due to its anisotropic dielectric constant. Finally, it undergoes a phase transition resulting in twinning and strain. While MgO has a low dielectric constant (10-12) it provides a poor lattice match to high temperature superconductors (HTSC) resulting in a mismatch of as much as 7%. Sapphire has a very large and anisotropic dielectric constant resulting in very difficult device calculations.

Recently, we have been investigating antimonates with ordered perovskite structures because they have relatively low dielectric loss (10^{-3}) and low isotropic dielectric constants [6,7]. In this paper we report on the deposition of thin film compounds by pulsed laser deposition in the antimonate system $\text{A}_4\text{MeSb}_3\text{O}_{12}$, where A= barium (Ba), strontium (Sr) and Me= lithium (Li), sodium (Na) and potassium (K). The crystal structures of the compounds in the system barium Me antimonate ($\text{Ba}_4\text{MeSb}_3\text{O}_{12}$), where Me=Li and Na, have been previously determined by x-ray and neutron diffraction [8-10]. Both Li and Na compounds are cubic, $\text{Im}\bar{3}\text{m}$ perovskites and exhibit a Me:Sb ordering of 1:3 on octahedral (B) sites. Strontium sodium antimonate ($\text{Sr}_4\text{NaSb}_3\text{O}_{12}$) has been reported to be monoclinic $\text{P}2_1/\text{n}$ as determined from x-ray and neutron diffraction studies [11]. This is in contrast to what we have found.

EXPERIMENTAL

Bulk compounds were prepared by solid state reaction between reagent grade barium carbonate (BaCO_3), strontium carbonate (SrCO_3), lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and antimony trioxide (Sb_2O_3) by reacting intimate mixtures of stoichiometric amounts of each. Components were ground together in a mortar, the resulting mixture was pressed into discs and heated to 1100°C (rate= 180°C/hr) for 15 hours in air, cooled to 100°C at the same rate, and removed from the furnace. The disc was reground to a powder with a particle size of $100\mu\text{m}$ or less, pressed into 1-1/4 inch discs between 1/8 and 1/4 inch thick in a steel die, then repressed isostatically at 60000 psi, sintered at $1450\text{-}1600^\circ\text{C}$ for 20-50 hours, cooled to 100°C and removed from the furnace. The discs after sintering were about one inch in diameter. Lattice parameters were obtained from diffractometer scans taken between $15\text{-}155^\circ 2\theta$ using $\text{CuK}\alpha$ radiation ($\lambda=1.5405\text{ \AA}$) or $\text{FeK}\alpha$ ($\lambda=1.93604$) using a least squares fit to the Nelson-Riley [12] function for the last 15 diffraction peaks.

Density measurements were obtained with a helium gas pycnometer on Sintered bulk discs. Earlier investigators prepared some of these compounds by firing samples between 1000 and 1400° C [8--10]. We found that sintering temperatures between 1550-1600° C were required to achieve very dense samples. Such samples were essential for complex dielectric measurements. Experimental densities are compared with x-ray densities in Table 1.

TABLE 1. PROPERTIES of $A_4MeSb_3O_{12}$ COMPOUNDS

| COMPOUND | SINTERING TEMP (°C) | LATTICE PARAMETER A | | DENSITY (g/cm ³) | | DIELECTRIC | |
|---|------------------------|---------------------|---|------------------------------|------|------------|-------------------------|
| | | THIS WORK | LITERATURE | X-ray | Exp. | CONST | LOSS 10 ³ |
| Sr ₄ NaSbO ₁₂ | 1450 | 8.180 | 8.0792 [11] (a=8.0913) (b=8.0871) (c=8.0918) (b=89.953) | 5.52 | 5.60 | 11.5 | 9.0 |
| Sr ₄ KSb ₃ O ₁₂ | 1450 | 8.23* | | | 6.72 | 9.0 | 2.5 |
| Ba ₄ LiSb ₃ O ₁₂ | 1450 | 8.221 | 8.217 [8] | 6.65 | 6.62 | 16.2 | 0.5 |
| Ba ₄ NaSb ₃ O ₁₂ | 1450 | 8.275 | 8.273(4) [10] | 6.62 | 6.64 | 14.4 | 0.6 |

*pseudo cubic

Microwave measurements of the real and imaginary parts of the dielectric constant were performed at approximately 9.32 and 10.0 GHz at room temperature. A detailed account of the experimental equipment and procedure may be found elsewhere [7]. The dielectric data for each compound may be found in Table 1. The sintered discs were also employed as targets for deposition of thin films by pulsed laser ablation deposition (PLD). A KrF excimer laser ($\lambda=248$ nm) was employed for deposition using a pulse repetition rate of 10 Hz and a laser fluence of 1-2 J/cm² at the target; other deposition parameters for each sample are given in Table 2.

TABLE 2. DEPOSITION PARAMETERS

| COMPOUNDS | OXYGEN PRESSURE (m Torr) | HEATER BLOCK TEMP. (°C) |
|---|-----------------------------|----------------------------|
| Sr ₄ NaSb ₃ O ₁₂ | 80 | 720 |
| Sr ₄ KSb ₃ O ₁₂ | 170 | 800 |
| Ba ₄ LiSb ₃ O ₁₂ | 170 | 800 |
| Ba ₄ NaSb ₃ O ₁₂ | 80 | 720 |

RESULTS

All the Ba compounds are cream in color as previously reported [8]. X-ray diffraction patterns were indexed as body-centered cubic consistent with the literature, and lattice parameters are in good agreement with the literature. $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ is also cream colored. An x-ray diffraction powder pattern was indexed as face-centered cubic. Woodward et al. [13] have described in the series $\text{A}_2\text{M}^{3+}\text{M}^{5+}_6$ face-centered cubic perovskites a subcell based on hkl reflections all even and a supercell based on hkl all odd reflections arising as a consequence of long range order. We observe a similar subcell and supercell in $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ and, as was observed by Woodward et al., the lattice parameter for the supercell is smaller than that of the subcell. The intensities of the diffraction peaks of the supercell are much weaker than those of the subcell.

Analysis of x-ray diffraction data obtained from films of $\text{A}_4\text{MeSb}_3\text{O}_{12}$ on YBCO (001)/MgO (100) reveals a predominant epitaxial relationship: $\text{A}_4\text{MeSb}_3\text{O}_{12}$ (h00)/YBCO (001)/MgO (100). A second weaker relationship $\text{A}_4\text{MeSb}_3\text{O}_{12}$ (hh0)/YBCO (001)/MgO(100) is also present (see Table 3). Strontium Potassium Antimonate ($\text{Sr}_4\text{KSb}_3\text{O}_{12}$) is not cubic. However, thin films prepared by PLD are highly oriented exhibiting the relationship: $\text{Sr}_4\text{KSb}_3\text{O}_{12}$ (220)/MgO (100). The observed dielectric constant and loss are in the same range as other antimonates previously investigated (see Table 1) [6,7].

TABLE 3. OBSERVED X-RAY REFLECTIONS

| STRUCTURE | MgO | YBCO | A4MeSb3O12 | INTENSITY |
|----------------------|-----|------|------------|-------------|
| Sr4KSb3O12/MgO | | | 200 | very weak |
| | | | | |
| | | | 220 | very strong |
| | | | 222 | very weak |
| | 200 | | | weak |
| | | | 440 | medium |
| | | | 444 | very weak |
| Sr4NaSb3O12/YBCO/MgO | | 002 | | weak |
| | | | 200 | weak |
| | | 003 | | medium |
| | | | 220 | very weak |
| | | 005 | | strong |
| | | | 400 | very strong |
| | | 006 | | strong |
| | | 007 | | very weak |
| Sr4KSb3O12/YBCO/MgO | | | 002 | strong |
| | | 003 | | medium |
| | | | 220 | weak |
| | | 005 | | strong |
| | 200 | | | very strong |
| | | | 400 | very strong |
| | | 006 | | strong |
| | | | 422 | very weak |
| | | 007 | | weak |
| | | | 442/600 | very weak |
| | | 009 | | very weak |
| | | 0010 | | very weak |
| | | | 800 | very weak |
| Ba4NaSb3O12/YBCO/MgO | | | 110 | weak |
| | | 002 | | medium |
| | | | 200 | medium |
| | | 003 | | medium |
| | | | 200 | weak |
| | | 005 | | medium |
| | 200 | | | very strong |
| | | | 400 | strong |
| | | 006 | | medium |
| | | 007 | | medium |
| | | 008 | | very weak |
| | | 009 | | very weak |
| Ba4LiSb3O12/YBCO/MgO | | | 200 | very weak |
| | | | 300 | weak |
| | | 111 | | very weak |
| | | | 211 | very weak |
| | | | 220 | very weak |
| | | 005 | | strong |
| | | | 400 | very strong |
| | 200 | | | very strong |
| | | 006 | | very strong |
| | | 007 | | medium |
| | | 008 | | weak |
| | | 009 | | weak |
| | | | 622 | weak |
| | | 0010 | | weak |
| | | 0011 | | weak |

CONCLUSION

If we consider the tolerance factor, $t = (r_A + r_O) / \sqrt{2} (r_B + r_O)$ where r_A and r_B are the radii of the A and B ions (Shannon and Prewitt crystal radii [14]), for all Ba compounds the ratios are about 1 or greater and between 1.0 and 0.9 for the Sr compounds. One might expect distortion from the cubic system but this does not occur until the alkali metal K. The difference in charge between B site ions is 4+, which is a major driving force for ordering as predicted by Galasso et al. [15]. $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ crystallizes as a monoclinic phase when prepared between 680 and 94° C. Analysis of x-ray data suggests a cubic body-centered structure [11]. Why then does $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ crystallize with a cubic face-centered structure when prepared above 1450° C, while barium sodium antimonate ($\text{Ba}_4\text{NaSb}_3\text{O}_{12}$), prepared at the same temperature, crystallizes with a body-centered structure similar to the low temperature form of $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$? An obvious explanation arises from a comparison of the size of Ba^{2+} and Sr^{2+} . Since Sr^{2+} is smaller, the B-B distances are more compressed, changing the ordering energy of Me^{1+} and Sb^{5+} , which produces the difference.

$\text{A}_4\text{MeSb}_3\text{O}_{12}$ compounds provide one advantage over other antimonates previously investigated. While $\text{Sr}_2\text{GaSbO}_6$ and $\text{Sr}_2\text{ScSbO}_6$ provided a better lattice match to YBCO, $\text{A}_4\text{NaSb}_3\text{O}_{12}$ compounds afford better chemistry. In either case, diffusion of B site ions across the substrate/buffer layer interface will lead to substitution in YBCO films. In the case of Sc and Ga this results in a reduction in T_c when they substitute for Cu. However, Li, Na and K have all been reported to have no effect or increase on T_c and J_c , when present in small concentrations, depending upon the substituent site [16-19]. The use of $\text{A}_4\text{MeSb}_3\text{O}_{12}$ compounds as substrates/buffers turns a detriment, diffusion of ions across an interface, into an advantage.

REFERENCES

1. P.W. Chu, Scientific American, **273** 162 (1986).
2. E. Belohoubek, D. Kalokitis, A. Fathy, E. Denlinger, A. Pique, X.D. Wu, S.M.Green and T.Venkatesen, Appl. Superconductivity **1**, 1555 (1993)
3. J. Talvacchio and G.R. Wagner, SPIE **22**, 1292 (1990).
4. N. Newman and W.G. Lyons, J. Supercond. **6**,119 (1993).
5. J.M. Philips, M.P. Siegal, R.V. van Dover, T.H. Tiefel, J.H. Marshall, C.D. Brandle, G. Berkstresser, A.J. Strauss, R.E. Fahey, S. Sengupta, A. Cassanho and H.P. Jenssen, J.Mater. Res. **7**, 2650 (1992).
6. A. Tauber, R.D. Finnegan, S.C. Tidrow, W.C. and D.W. Eckart, presented at the 1994 MRS Fall Meeting, Boston, MA,1994 (unpublished).
7. S.C. Tidrow, A. Tauber, R.D. Finnegan and W.D. Wilber, presented at the 1995 MRS Spring Meeting, San Francisco, CA, 1995 (in press, Physica C).
8. A.J. Jacobson, B.M. Collins and B.E.F. Fender, Acta Cryst. B. **30**, 1705 (1974).
9. J.A. Alonso, E. Mzayek, I. Rasines, Mat. Res. Bull. **22**, 6969 (1987).
10. K.P. Reis and A.J. Jacobson, Acta Cryst. C, **49**, 1585 (1993).
11. J.A. Alonso, E. Mzayek and I. Rasines, J. Solid State Chem. **84**, 1622 (1990).
12. B.D. Cullity, Elements of X-ray Diffraction, (Addison-Wesley Publishing Co.Inc, Reading, 1978), p.366.
13. P. Woodward, R.D. Hoffmann, A.W. Sleight, J. Mater. Res., **9**, 210 (1994).
14. R.D. Shannon and C.T. Prewitt, Acta Cryst., B. **25**, 925 (1965).
15. F. Galasso and W. Darby, J. Phys. Chem. **66** 131 (1962).
16. J. Azoulay, A. Verdyan, I. Lapsker, Physica C, **235**, 597 (1994).
17. T Nurgaliev, S. Miteva, I. Nedkov, A.Veneva, M. Tsdlskov, J.Appl. Phys. **76**, 7118 (1994).
18. T. Suzuki, H. Okadu, T. Takeuchi, Sol. St. Comm. **77**, 587 (1991).
19. T. Suzuki, T. Yamazaki, R. Sekine, A. Oukitu and H. Seki J. Mat. Sci. Letts. **8**, 1271 (1989).

ARMY RESEARCH LABORATORY
PHYSICAL SCIENCES DIRECTORATE
MANDATORY DISTRIBUTION LIST

August 1995
Page 1 of 2

Defense Technical Information Center*
ATTN: DTIC-OCC
8725 John J. Kingman Rd, STE 0944
Fort Belvoir, VA 22060-6218
(*Note: Two DTIC copies will be sent
from STINFO office, Ft. Monmouth, NJ)

Advisory Group on Electron Devices
ATTN: Documents
Crystal Square 4
1745 Jefferson Davis Hwy, Suite 500
(2) Arlington, VA 22202

- Director
US Army Material Systems Analysis Actv
ATTN: DRXSY-MP
(1) Aberdeen Proving Ground, MD 21005

Commander, CECOM
R&D Technical Library
Fort Monmouth, NJ 07703-5703
(1)AMSEL-IM-BM-I-L-R (Tech Library)
(3) AMSEL-IM-BM-I-L-R (STINFO Ofc)

- Commander, AMC
ATTN: AMCDE-SE
5001 Eisenhower Avenue
(1) Alexandria, VA 22333-0001

- Director
Army Research Laboratory
ATTN: AMSRL-D (John W. Lyons)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

- Director
Army Research Laboratory
ATTN: AMSRL-DD (COL Thomas A. Dunn)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197
(1) AMSRL-OP-SD-TA (ARL Records Mgt)
(1) AMSRL-OP-SD-TA (ARL Tech Library)
(1) AMSRL-OP-SD-TP (ARL Tech Publ Br)

Directorate Executive
Army Research Laboratory
Physical Sciences Directorate
Fort Monmouth, NJ 07703-5601
(1) AMSRL-PS
(1) AMSRL-PS-T (M. Hayes)
(1) AMSRL-OP-FM-RM
(22) Originating Office

ARMY RESEARCH LABORATORY
PHYSICAL SCIENCES DIRECTORATE
SUPPLEMENTAL DISTRIBUTION LIST
(ELECTIVE)

August 1995
Page 2 of 2

- | | | | |
|-----|---|-----|---|
| (1) | Deputy for Science & Technology Office, Asst Sec Army (R&D) Washington, DC 20310 | (1) | Cdr. Marine Corps Liaison Office ATTN: AMSEL-LN-MC Fort Monmouth, NJ 07703-5033 |
| (1) | HQDA (DAMA-ARZ-D/ Dr. F.D. Verderame) Washington, DC 20310 | | |
| (1) | Director Naval Research Laboratory ATTN: Code 2627 Washington, DC 20375-5000 | | |
| (1) | USAF Rome Laboratory Technical Library, FL2810 ATTN: Documents Library Corridor W, STE 262, RL/SUL 26 Electronics Parkway, Bldg 106 Griffiss Air Force Base NY 13441-4514 | | |
| (1) | Dir, ARL Battlefield Environment Directorate ATTN: AMSRL-BE White Sands Missile Range NM 88002-5501 | | |
| (1) | Dir, ARL Sensors, Signatures, Signal & Information Processing Directorate (S3I) ATTN: AMSRL-SS 2800 Powder Mill Road Adelphi, MD 20783-1197 | | |
| (1) | Dir, CECOM Night Vision/ Electronic Sensors Directorate ATTN: AMSEL-RD-NV-D Fort Belvoir, VA 22060-5806 | | |
| (1) | Dir, CECOM Intelligence and Electronic Warfare Directorate ATTN: AMSEL-RD-IEW-D Vint Hill Farms Station Warrenton, VA 22186-5100 | | |